

PATENT SPECIFICATION



DRAWINGS ATTACHED

1,100,102

Date of Application and filing Complete Specification: 14 April, 1965.

No. 16055/65.

Application made in Japan (No. 23358) on 25 April, 1964.

Complete Specification Published: 24 Jan., 1968.

© Crown Copyright 1968.

Index at acceptance:—H1 BF

Int. Cl.:—H 01 m 27/00

COMPLETE SPECIFICATION

Fuel Cell Electrode

We, FUJI DENKI SEIZO KABUSHIKI KAISHA, a Japanese Body Corporate, of 1—1 Tanabe-Shinden, Kawasaki-shi, Japan, and NIPPON JUNSUISO KABUSHIKI KAISHA, a Japanese

5 Body Corporate, of 906 Iino Building, 22, 2-chome, Uchisaiwai-cho Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to fuel cell electrodes and more particularly to improvements in hydrogen permeable electrodes.

15 The "fuel cell" as used in the present specification, is an electro-chemical cell capable of generating electrical energy through electro-chemical combustion of fuel with oxidizing agents.

20 In general, the fuel cell usually consists of a fuel electrode, an electrolyte and an oxidizing electrode. A fuel gas such as hydrogen is circulated on one side of the fuel electrode and an oxidizing gas such as air is circulated on one side of the other electrode. In the case of an acid electrolyte fuel cell, the hydrogen diffuses in the electrolyte passing through the fuel electrode and a hydrogen molecule is divided into two hydrogen ions and two electrons

30 which flow into the oxidizing electrode through the external electrical circuit.

On the other hand, an oxygen molecule receives at the oxidizing electrode four electrons from the external electrical circuit forming two molecules of water in combination with four hydrogen ions. Thus, according to the external electron flow from the fuel electrode into the oxidizing electrode through the external electrical circuit, the oxidizing electrode and the fuel electrode respectively constitute the positive electrode and the negative electrode.

40 In the past it was conventional to employ a porous metallic body as the electrode for the fuel cell, for example British Patent No.

910,495. However it was difficult to regulate the three-phase interface of solid-gas-electrolyte by a suitable combination of pore size of the electrode, differential pressure of the gas, and surface tension of the electrolyte.

50

To solve this problem a non-porous hydrogen diffusion electrode made of palladium membrane was proposed. Since a non-porous palladium membrane electrode allows the permeation to hydrogen selectively, a stable electro-chemical reaction zone is built at the outlet side (electrolyte side) of the membrane, irrelevant to the gas pressure applied.

55

At this point the non-porous membrane electrode is superior to the porous electrode. On the other hand, the maximum current density obtainable from such hydrogen permeable membrane electrode is limited by the permeation rate of hydrogen through said membrane electrode. The permeation rate increases with increased temperature, increased pressure applied and decreased thickness of the membrane. Consequently, to obtain a high current drain from such membrane electrode high-temperature and high-pressure operation, for example, 700° C., 30 kg/cm², with a thin membrane may also be needed. Therefore, the tensile strength of the membrane must be large enough to stand at the operating conditions.

60

70 However, it has been found that these hydrogen permeable membranes made of pure palladium have a poorer tensile strength at high temperature (e.g. 700 kg/cm² at 500° C.) and moreover tend to absorb a large amount of hydrogen below 150° C., and to produce a brittle β-phase palladium hydride.

65

75 Now, the palladium-silver alloy membranes specified in the British Patent No. 928,499 retain superior characteristics in brittleness at the lower temperature, however, they are still poorly resistant to corrosion and exhibit a lowering of tensile strength, which makes impossible a pressurized operation, at

80

85

90

[Price 4s. 6d.]

a temperature higher than 400° C. In particular, the material is not recommended for the hydrogen permeable electrode of a fuel cell which substantially uses a molten carbonate mixture as electrolyte at an operating temperature higher than 400° C.

Also, when such hydrogen-containing fuel gases as dissociated ammonium gas or the mixture of gases obtained from the steam reforming of hydrocarbons are employed instead of pure hydrogen, the palladium-silver alloy membrane electrode behaves electrochemically as in the case when pure hydrogen is used as fuel, but is not satisfactory for long time use due to its poor anti-corrosion property against steam or undissociated ammonia gas contained in the fuel gas mixture, having a temperature higher than 400° C.

Moreover, when the said palladium-silver alloy is exposed at a temperature higher than 500° C. for a long period, recrystallization which deteriorates the mechanical property of the alloy occurs.

A principal object of the present invention is therefore to provide a hydrogen permeable electrode having a high permeability to hydrogen as a fuel gas and retaining high tensile strength even at high temperature.

Another object of the present invention is to provide a hydrogen permeable electrode which has high corrosion resistance against electrolytes such as molten carbonate mixture.

Still another object of the present invention is to provide a fuel electrode having a high corrosion resistance against ammonia and steam contained in fuel gas at a temperature higher than 400° C.

Still another object of the present invention is to provide a hydrogen permeable electrode which does not form excessively a brittle β -phase palladium hydride even at lower temperature.

Still another object is to provide a hydrogen permeable electrode which has a recrystallization temperature higher than 700° C. and therefore exhibits mechanical stability even in prolonged operation at a temperature up to 700°C.

In order to accomplish these objects as aforementioned, the fuel cell electrode of this invention consists of an alloy membrane which is composed of palladium and at least one element selected from Group Ib of the Periodic Table and at least one element from Group VIII of the Periodic Table other than palladium, in which said element selected from Group Ib is contained in an amount of 2—40%, said element selected from Group VIII is contained in an amount of 0.1—20%, and said palladium is contained in an amount of at least 60%.

The term "membrane" as used in the present invention means principally a flat or corrugated plate having a thickness ranging from about 0.001 to about 0.5 mm., or a tube

having a wall thickness within said range.

The aforementioned alloy was developed for hydrogen purifying devices and was disclosed in the British Patent No. 964,532, in which, however, no reference was made to the fuel cell electrodes.

We have used the abovementioned alloys for fuel cell electrodes and have discovered that the alloys show superior characteristics when utilised as fuel electrodes especially in high-temperature-type fuel cells.

Palladium alloys as described in the present invention have a hydrogen permeability about 34—140% larger than that of the pure palladium or palladium-silver alloy and therefore have a larger current-carrying capability as utilised for the fuel electrodes.

In addition, the tensile strength thereof at 500° C. also shows a value about 100% greater than that of the conventional electrodes.

Accordingly, a hydrogen permeable membrane electrode made of said alloys withstands high temperature and high-pressure operation, so that said electrode is further capable of carrying an unusually large current density, for example 2 A/cm².

Furthermore, the present alloy has not only a high corrosion resistance against the high temperature gaseous materials such as steam or ammonia but also has a distinct slowness of crystal growth up to 700° C. Consequently, the change of mechanical properties caused by recrystallisation of the alloy does not result.

These improvements are developed only by suitable combinations of the alloying components (Group Ib and VIII elements). An addition of more than 2% of Group Ib metals to palladium generally enhances the permeation rate of hydrogen through the resultant alloy, but the addition of more than 40% decreases the permeation rate.

Further, the maximum a permeation rate generally exists in a composition range of about 20—35% silver in the case of silver-palladium alloy and about 5—20% gold in the case of gold-palladium alloy. When silver and gold are employed in combination, the preferred range of total amount of Group Ib elements is also about 20—35% of the resultant Pd-Ag-Au alloy.

On the other hand an addition of elements from Group VIII, such as platinum, rhodium or ruthenium to palladium, also somewhat enhances the permeation rate of hydrogen.

Moreover said addition promotes a distinct increase in tensile strength and an increase in corrosion resistance, and the recrystallisation temperature is thereby raised up to about 700° C.

The aforesaid effects appear in a range of composition comprising 0.1—20% Group VIII elements, however an addition of more than 5% Group VIII elements generally

70

75

80

85

90

95

100

105

110

115

120

125

130

decreases the hydrogen permeation rate of the resultant alloy, and makes it difficult to roll or to shape said alloy. Therefore a preferred range of the composition for Group VIII elements is 0.1—5%.

Also Group VIII elements other than Pt-group, such as Fe, Ni and Co, principally act as a suppressor of recrystallisation of Pd-alloys, consequently they are also recommended as an alloying component for the present invention.

When said Group Ib elements and Group VIII elements are added to palladium at the same time to compose an alloy, their effects are not contradictory to each other. However, it must be noticed that the palladium content of an alloy is to exceed 60%, because the hydrogen permeation rate is substantially lowered in an alloy containing less than 60% palladium.

As is apparent from the above described illustrations, the alloys employed as electrodes of the present invention possess aforementioned superior properties such as a high permeability to hydrogen (i.e. a large current carrying capability), a high tensile strength which enables a pressurised operation, for example at 30 kg/cm² hydrogen, even at 500°—700° C., as well as a high corrosion resistance and mechanical stability.

Embodiments of the present invention will now be described with reference to the accompanying drawings, in which:

Figure 1 is a testing device for measuring the corrosion resistance of the hydrogen permeable electrode against the molten carbonate electrolyte.

Figure 2 is a device for testing the electrochemical characteristics of an alloy membrane electrode according to the present invention.

Figure 3 shows current-potential curves

which represent the electrochemical property of the alloy membrane hydrogen electrode according to the present invention.

Figure 4 is a cross sectional view of a fuel cell incorporating a fuel electrode according to the present invention.

Referring now to Figure 1, an alloy membrane 11 of approximately 2 cm² surface area, to which a gold wire (0.2 mm diameter) 14 is spot-welded, is applied to the test for measuring corrosion resistance against a molten alkali carbonate electrolyte. Said electrolyte mixture 13 consisting of lithium carbonate (Li₂CO₃), sodium carbonate (Na₂CO₃) and potassium carbonate (K₂CO₃) in 4:3:3 mole ratio is filled in a gold crucible 12, and test piece 11 is dipped therein.

A gold wire 15 is connected to the gold crucible 12 and a D.C. power supply 16, variable resistor 17 and ampere meter 18 are connected in series between the wires 14 and 15.

Now the crucible 12 is put into a furnace continuously fed with carbon dioxide gas and heated up to melt the carbonate mixture 13. After the predetermined temperature is reached, an electric current is applied between the test piece 11 and the crucible 12. Said test piece 11 is taken out after definite time in order to measure weight loss or gain and to observe surfacial changes.

The present experimental test was carried out for one hour at an electrolyte temperature of 800° C., an electrolytic current density of 100 MA/cm² based upon the surface area of said electrode and an electrolyzing period of one hour. The experimental results obtained from various kinds of alloys according to the present invention are set out in the Table 1, for comparative purpose with the case of palladium, silver and palladium-silver alloy.

TABLE 1

	Alloy composition (Weight %)	Weight Change (mg/cm ² /AH)	Surficial State
Present Invention	Pd 65, Ag 28, Au 5, Ru 2	-0.9	Slightly etched
	Pd 70, Au 25, Rh 5	±0.0	Scarcely changed
	Pd 68, Ag 30, Ru 2	-1.3	A little etched
	Pd 65, Ag 10, Au 20, Pt 1	+0.2	Grey coloured
	Rh 2, Ru 1.8, Fe 0.2		
Reference	Pd	-2.0	Etched with grey colour
	Ag	-2400.0	Dissolved at about 60% current efficiency
	Pd 75, Ag 25	-31.5	Bluish-grey coloured

Since palladium alloy membranes disclosed in the present invention are, as is apparent from the above exemplified table, substantially unchanged by the anodic current charged in the molten carbonate mixture, the present alloy membranes therefore effectively perform as a hydrogen permeable electrode for the prolonged use, while the palladium-silver alloy membrane specified in the British Patent No. 928,499 is subjected to corrosion and is not practical in use.

The Table 2 shows the testing results of

the maximum electric currents obtainable from the hydrogen permeable membrane electrode consisting of various kinds of alloys in accordance with the present invention, and of other alloys (marked with *) for comparison, all of which were measured by using an experimental cell device of Figure 2 with the eutectic alkali carbonate mixture consisting of Li_2CO_3 , Na_2CO_3 and K_2CO_3 in 4:3:3 mole ratio under 1 kg/cm² hydrogen pressure at 420°C.

15

20

TABLE 2

No.	Group Ib			Group VIII				Current (mA/cm ²)
	Pd	Ag	Au	Pt	Rh	Ru	Fe	
1*	100							330
2	60	38		2				390
3	65	30		5				660
4	65	25		10				485
5	65	15		20				340
6	75	5		20				320
7	88		10			2		730
8	93		5			2		670
9	96		2			2		430
10*	97		1			2		340
11	70	20	5		5			670
12	73	20	5		2			660
13	74.5	20	5		0.5			645
14	74.8	20	5		0.2			645
15*	75	20	5					654

25 High current density can particularly be expected for alloys containing 20—35% silver (together with or without gold) or 5—20% gold, and 0.1—5% elements selected from Group VIII other than palladium.

30 There will now be described some examples according to the present invention.

The present invention is not to be limited by the illustrated examples and it is possible to produce still other embodiments without departing from the scope of the present invention.

EXAMPLE 1.

A hydrogen permeable electrode was constructed as a non-porous membrane with 0.15 mm thickness consisting of a four component alloy such as 65% palladium, 28% silver, 5% gold and 2% ruthenium. Although this four-component alloy membrane absorbed 0.33 atomic hydrogen per atom metal at room temperature, no β -phase hydride was formed. Further, when there was a differential pressure such as 3 kg/cm² between inlet and outlet side of the alloy membrane, the

40

45

hydrogen permeated at a rate of $4.8 \text{ cm}^3/\text{cm}^2 \cdot \text{min}$. through the membrane at which stage the tensile strength of the membrane was $1,500 \text{ kg/cm}^2$ at 500°C .

- 5 The polarisation of the said alloy membrane electrode was further examined by using it in the experimental fuel cell as specified in Figure 2. In Figure 2, a hydrogen permeable membrane 21 is gas and liquid tightly, held
 10 in a housing 22 consisting of refractory and insulating materials. Said housing 22 is divided into two chambers such as gas-chamber A and electrolyte-chamber B.

To the chamber A, a fuel gas feed pipe 24
 15 and an exhaust pipe (not shown in the drawing) are provided, while on the opposite side of the membrane electrode 21 in the chamber B, a counter electrode 23 consisting of a palladium-gold alloy is provided. From the
 20 upper part of the chamber B, a reference electrode 30 constituted by a ceramic pipe 25 in which a silver wire 26 is held, is inserted into the chamber B which is filled up with the eutectic alkali carbonate mixture 29 consisting
 25 of Li_2CO_3 , Na_2CO_3 and K_2CO_3 in 7:5:4 mole ratio. Said carbonate mixture 29 melts at about 400°C . and performs as electrolyte. The distance between the hydrogen permeable electrode 21 and the counter electrode
 30 23 is 3 cm, and the distance between the reference electrode 30 and the hydrogen permeable electrode 21 is 1 cm.

Connecting wires 27 and 28 are respectively connected to the electrode 21 and the counter electrode 23. Between the wires 27 and 28, an external D.C. power supply 31, a variable resistor 32 and an ammeter 33 are connected and the silver wire 26 extended from the reference electrode 30 is connected
 40 to the electrode 21 through a voltmeter 34.

Now, the aforesaid cell was assembled in a furnace fed with carbon dioxide gas, and hydrogen having 0.5 kg/cm^2 pressure was supplied into the chamber A from the fuel gas
 45 conducting pipe 24. At the same time, a mixture gas consisting of oxygen and carbon dioxide gas in the proportion of 1:1 in volume was supplied into the chamber B through the pipe 25. At this stage, a potential
 50 difference appeared between the hydrogen permeable electrode 21 and reference electrode 30 which was measured on open circuit. Thereafter different anodic currents were applied to the hydrogen permeable electrode
 55 21 through the external D.C. power supply 31, to determine corresponding polarisations.

The polarisation curves thus obtained are shown in Figure 3. In Figure 3, the curve *a* shows a polarisation curve at 500°C , the
 60 curve *b* shows another polarisation curve at 700°C .

As is seen from the aforementioned Figure 3, the current-potential curves thereof are mostly linear and exhibits substantially an ohmic nature.

On the other hand, in the case that a hydrogen permeable membrane electrode of 0.15 mm thickness substantially consisting of 75% palladium and 25% silver was tested at 500°C . under 3 kg/cm^2 differential pressure, the hydrogen permeability rate of the membrane electrode reached to $4.0 \text{ cm}^3/\text{cm}^2 \cdot \text{min}$. and the tensile strength thereof was $800 \text{ kg}/\text{cm}^2$.

The above mentioned hydrogen permeable membrane electrode was assembled in the experimental cell device mentioned in Figure 2 and tested under the same condition as the previous example.

The result thereof is also shown by the curve *c* in Figure 3. The curve *c* shows non-linear portions. Further, the polarisation curve *d* was observed in the case that the tubular hydrogen permeable electrode having a diameter of 3.0 mm and a thickness of 0.1 mm with composition of 25% silver and 75% palladium was operated at 7 kg/cm^2 differential pressure of hydrogen using a potassium hydroxide-sodium hydroxide eutectic at 250°C . as electrolyte.

It will now be apparent from Fig. 3 that the present invention is far superior by comparison of curves *a,b* and *c,d*.

Although the superior result of the aforementioned example of this invention has been achieved for case in which a low pressure of hydrogen such as 0.5 kg/cm^2 was applied, further improvements of the discharge characteristics is made by increasing the supplying pressure of hydrogen since the present alloy membrane has a greater value of tensile strength. The improvement of the discharge characteristics of the conventional palladium-silver alloy by increasing pressure is limited due to its poor tensile strength.

EXAMPLE 2.

A tubular alloy membrane having 2 mm (diameter) \times 0.06 mm (thickness) \times 20 cm (length) composed of 65% palladium, 10% silver, 20% gold, 1% platinum, 2% rhodium, 1.8% ruthenium and 0.2% iron was applied as a fuel electrode of the fuel cell mentioned in Figure 4.

The abovementioned seven-component alloy membrane absorbs 0.32 atomic hydrogen per atom metal at room temperature and does not form β -phase hydride.

Further, said seven-component alloy membrane has a hydrogen permeability rate 15% larger than that of the alloy membrane of to Example 1. The tensile strength thereof is as high as 1950 kg/cm^2 at 500°C . and the alloy retains a fine crystalline structure and does not recrystallise under exposure at high temperature for a long period.

In Figure 4, 43 is a tubular hydrogen permeable fuel electrode comprising the severe component alloy. Said hydrogen permeable fuel electrode 43 is provided with a purge-

70

75

80

85

90

95

100

105

110

115

120

125

- 5 pipe 46 and the necessary fuel is applied from the conducting pipe 41 through a joint 42. A pasty electrolyte 44 consists of magnesium oxide powder which keeps the molten mixture of alkali carbonates in position. An air electrode is then formed by winding a silver gauze 45 around the electrolyte 44 which is made to adhere on the outer surface of the fuel electrode 43 having a thickness of 2 mm.
- 10 If the air containing carbon dioxide gas was made to flow over the outer surface of the cell, and hydrogen having 1.0 kg/cm² pressure was supplied into the fuel electrode provided in the cell, an open circuit voltage of the cell presented 1.02 volt at 700° C.
- 15

The terminal voltage measured at the discharge current of 0.6 ampere was 0.95 volt, while, 0.83 volt was shown in the case of 2.6 ampere. The drop of the terminal voltage is considered to be caused by polarisation of the air electrode and the resistance of the electrolyte. Since the fuel cell characteristics of the present experiment is principally determined by factors other than the fuel electrode, increasing of the hydrogen pressure is not particularly necessary, however, said tube may well stand against an internal pressure of 30 kg/cm² at 700° C. Further, 1.03 volts terminal voltage were produced when 2.6 kg/cm² dissociated ammonia gas was supplied into the fuel electrode at 500° C. The terminal voltage at 0.6 ampere discharge current was 0.90 volt, when 5% of the supplying fuel gases was continuously purged.

35 In addition, even after the cell had been operated continuously for 24 hours with the above condition, no change of characteristics was observed.

WHAT WE CLAIM IS:—

- 40 1. A hydrogen permeable membrane electrode for fuel cells consisting of an alloy composed of palladium and at least one element selected from Group Ib of the Periodic Table and at least one element selected from Group VIII of the Periodic Table other than palladium, in which said element selected from Group Ib is contained in an amount of 2—39.9%, said element selected from Group VIII is contained in an amount of 0.1—20%, and said palladium is contained in an amount of at least 60%.
- 45 2. A hydrogen permeable membrane electrode as claimed in Claim 1, consisting of an alloy substantially composed of 5—25% gold as an element selected from Group Ib, 0.1—5% ruthenium as an element selected from Group VIII and the balance palladium.
- 50 3. A hydrogen permeable membrane electrode as claimed in Claim 1, consisting of an alloy substantially composed of 5—25% gold as an element selected from Group Ib and 0.1

to 5% platinum as an element selected from Group VIII and the balance palladium.

4. A hydrogen permeable membrane electrode as claimed in Claim 1, consisting of an alloy composed of 5—25% gold as an element selected from Group Ib, 0.1—5% rhodium as an element selected from Group VIII and the balance palladium.

5. A hydrogen permeable membrane electrode as claimed in Claim 1, consisting of an alloy substantially composed of 20—35% silver as an element selected from Group Ib, 0.1—5% ruthenium as an element selected from Group VIII and the balance palladium.

6. A hydrogen permeable membrane electrode as claimed in Claim 1, consisting of an alloy substantially composed of 20—35% silver as an element selected from Group Ib, 0.1—5% platinum as an element selected from Group VIII and the balance palladium.

7. A hydrogen permeable membrane electrode as claimed in Claim 1, consisting of an alloy substantially composed of 20—35% silver as an element selected from Group Ib, 0.1—5% rhodium as an element selected from Group VIII and the balance palladium.

8. A hydrogen permeable membrane electrode as claimed in Claim 1, consisting of an alloy substantially composed of 20—35% mixture comprising silver and gold as the element selected from Group Ib, 0.1—5% ruthenium as an element selected from Group VIII and the balance palladium.

9. A hydrogen permeable membrane electrode as claimed in Claim 1, consisting of an alloy substantially composed of 20—35% mixture comprising silver and gold as the elements selected from Group Ib, 0.1—5% platinum as an element selected from Group VIII and the balance palladium.

10. A hydrogen permeable membrane electrode as claimed in Claim 1, consisting of an alloy substantially composed of 20—35% mixture comprising silver and gold as the elements selected from Group VIII, 0.1—5% rhodium as the element selected from Group VIII, and the balance palladium.

11. A hydrogen permeable membrane electrode as claimed in Claim 1, consisting of an alloy substantially composed of 28% silver, 5% gold, 2% ruthenium and the balance palladium.

12. A hydrogen permeable membrane electrode as claimed in Claim 1, consisting of an alloy substantially composed of 10% silver, 20% gold, 1% platinum, 2% rhodium, 1.8% ruthenium, 0.2% iron and the balance palladium.

13. A fuel electrode as claimed in Claim 1 and substantially as hereinbefore described and as shown in the accompanying drawings.

65

70

75

80

85

90

95

100

105

110

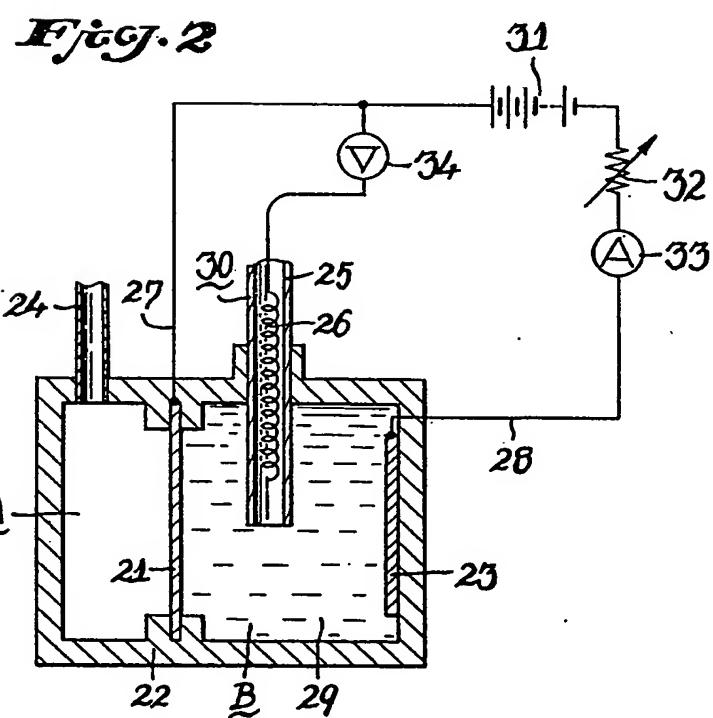
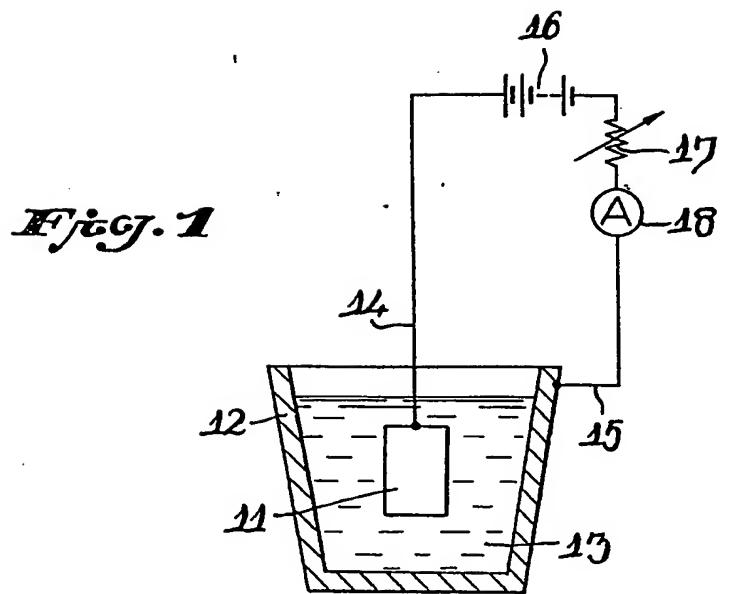
115

120

14. A fuel cell comprising at least one fuel electrode as claimed in any one of the preceding Claims and at least one oxidizing electrode.

For the Applicants:—
F. J. CLEVELAND & COMPANY,
Chartered Patent Agents,
Lincoln's Inn Chambers,
40—43, Chancery Lane, London, W.C.2.

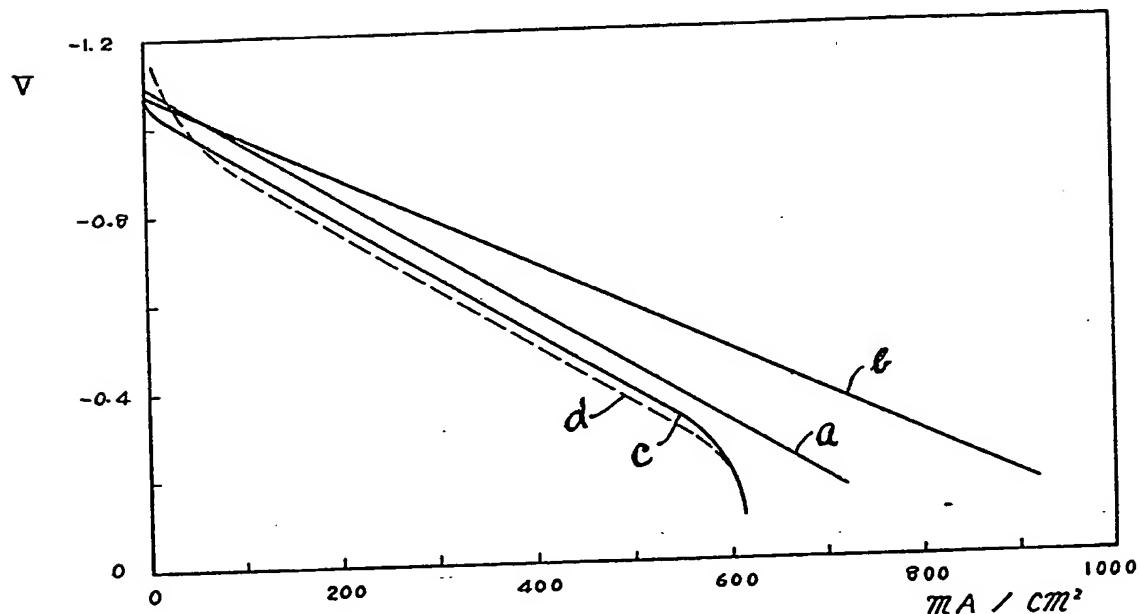
Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.
—1968. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2,
from which copies may be obtained.



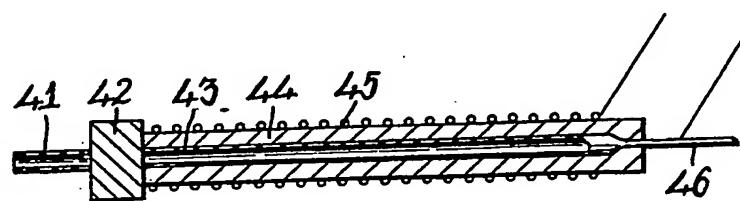
1,100,102
2 SHEETS

COMPLETE SPECIFICATION
This drawing is a reproduction of
the Original on a reduced scale.
SHEETS 1 & 2

Fjig. 3



Fjig. 4



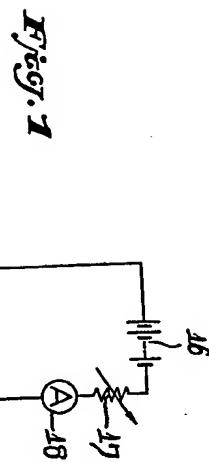
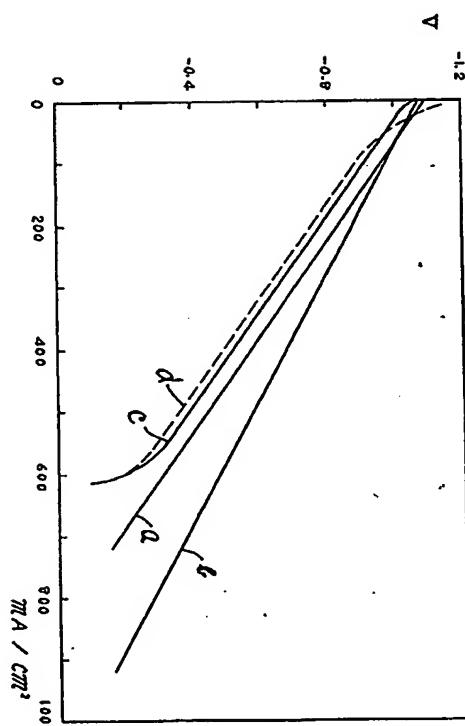


Fig. 1



V

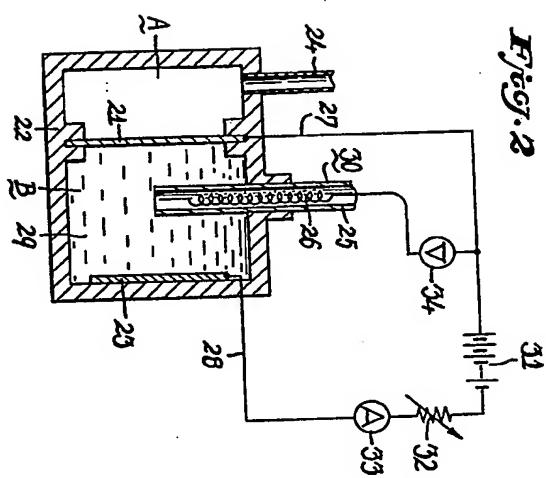


Fig. 2

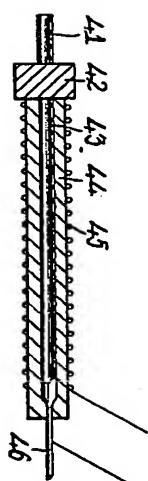


Fig. 4